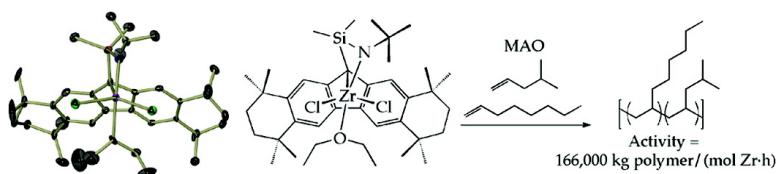


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Levi J. Irwin, Joseph H. Reibenspies, and Stephen A. Miller

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A Sterically Expanded “Constrained Geometry Catalyst” for Highly Active Olefin Polymerization and Copolymerization: An Unyielding Comonomer Effect

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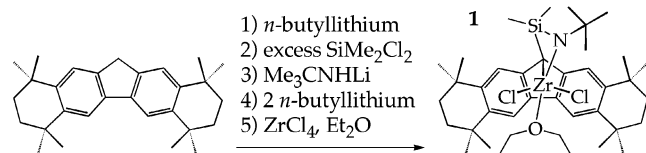
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received September 2, 2004; E-mail: samiller@mail.chem.tamu.edu

Constrained geometry catalysts (CGCs) have received considerable attention because of their ability to copolymerize ethylene with α -olefins,^{1–6} forming linear low-density polyethylene (LLDPE) on the commercial scale of over one billion kg per year. Reportedly, α -olefin incorporation exceeds that with other organometallic catalyst systems because of the steric accessibility afforded by the linked cyclopentadienyl–amido ancillary ligand. Although the precatalyst $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^1\text{-N-}i\text{Bu})\text{TiMe}_2$ is considered to be the commercial standard for ethylene/1-octene copolymerizations,⁷ it has been shown that indenyl–amido CGC systems such as $\text{Me}_2\text{-Si}(\eta^5\text{-2-Me-benz[e]Ind})(\eta^1\text{-N-}i\text{Bu})\text{TiCl}_2/\text{MAO}$ ⁸ (MAO = methylaluminumoxane) can induce high activity and moderate α -olefin incorporation in ethylene/1-octene copolymerizations. In contrast, existing fluorenyl–amido polymerization systems such as $\text{Me}_2\text{Si}(\eta^5\text{-C}_{13}\text{H}_8)(\eta^1\text{-N-}i\text{Bu})\text{TiCl}_2/\text{MAO}$ are typically inferior with respect to activity, comonomer incorporation, molecular weight, thermal sensitivity, and catalytic lifetime.^{6,9}

Herein we report the synthesis and initial MAO-cocatalyzed polymerization and copolymerization results of $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}i\text{Bu})\text{ZrCl}_2\cdot\text{OEt}_2$ (**1**), a sterically expanded zirconium fluorenyl–amido complex with an activity and α -olefin incorporation ability far exceeding those of even most titanium systems. The unusual structure of this precatalyst is likely related to its high polymerization and copolymerization activity, thermal stability, propensity to incorporate bulky α -olefins at unprecedented levels, and ability to form generally inaccessible copolymers such as copoly(1-octene/4-methyl-1-pentene). The catalyst synthesis is facile and scalable, while the starting materials are accessible and inexpensive—making **1** an ideal candidate for commercial utilization. The synthesis of **1** is outlined in Scheme 1 and begins with octamethyloctahydrodibenzofluorene,¹⁰ a sterically augmented version of fluorene (14 vs 9 Å).

Scheme 1. Synthesis of $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}i\text{Bu})\text{ZrCl}_2\cdot\text{OEt}_2$ (**1**)



The X-ray structure of **1** is shown in Figure 1 and represents the most sterically open CGC reported to date.¹¹ Inspection of the interatomic distances between the Zr and the five-membered ring of the $\text{C}_{29}\text{H}_{36}$ fragment reveals that the Zr–C(1) bond (2.299(7) Å) is notably shorter than those in analogous systems, which range from 2.377(7) to 2.430(5) Å.⁹ The next shortest Zr–C distance is 2.731(6) Å (Zr–C(2)), which is most accurately described as only a weak interaction.¹² Thus, the $\text{C}_{29}\text{H}_{36}$ fragment is best categorized as a simple η^1 X-type ligand,¹³ and **1** is formally a 12-electron trigonal–bipyramidal organometallic complex having amido and

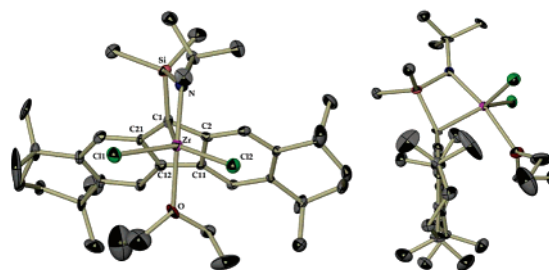


Figure 1. The structure of $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}i\text{Bu})\text{ZrCl}_2\cdot\text{OEt}_2$ (**1**) with 50% probability ellipsoids (frontal and side views, hydrogens omitted). Selected bond lengths (Å) and angles (deg): Zr–Cl(1) = 2.3918(18); Zr–Cl(2) = 2.4155(19); Zr–N = 2.013(5); Zr–O = 2.330(5); Cl–Zr–Cl = 112.92(7); Cl(1)–Zr–C = 110.87(18); Cl(2)–Zr–C = 136.16(18); C–Zr–N = 76.8(2); C–Zr–O = 93.40(18); N–Si–C = 95.3(3).

Table 1. Polymerization and Copolymerization Activities with **1**/MAO and **2**/MAO^a

monomer 1	concn (M)	monomer 2	concn (M)	activity ^b	
				1	2
ethylene	0.5	–	–	4,100 ^c	26,800 ^{c,d}
4-Me-P	7.54	–	–	27,800	2,900
1-octene	6.17	–	–	316,000	3,700
4-Me-P	7.54	ethylene	0.5	209,000	184,000
1-octene	6.17	ethylene	0.5	438,000	477,000 ^d
4-Me-P	3.62	1-octene	3.19	166,000	3,200

^a 1.66 μmol **1** or **2**; 1000 equiv MAO; $T_p = 75$ °C; 1.0 min; 26 mL total volume; solvent = toluene; 80 psi ethylene, where applicable; 4-Me-P = 4-methyl-1-pentene. ^b kg polymer/(mol M·h). ^c Average of three runs. ^d 0.5 min runs.

etheral ligands in the axial positions (N–Zr–O = 169.9°). As a consolation to the electron-deficient metal center, some stabilization is found in that the aromaticity of the aryl rings of the $\text{C}_{29}\text{H}_{36}$ moiety is not sacrificed—unlike the situation in all η^5 -fluorenyl ligands.

Table 1 reports that **1**/MAO is extremely effective in the homopolymerization of α -olefins. The activity in the homopolymerization of 4-methyl-1-pentene is about 10 times greater than that for $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^1\text{-N-}i\text{Bu})\text{TiCl}_2/\text{MAO}$ (**2**/MAO). The homopolymerization of 1-octene with **1**/MAO is strikingly efficient, converting 49% of the monomer to poly(1-octene) in one minute with an activity that is 85 times greater than that for **2**/MAO.

An unexpected result for **1**/MAO is that the observed activity for ethylene homopolymerization is the lowest. Correcting for monomer concentration, the first generation Ti-CGC **2**/MAO is 140 times more active for ethylene homopolymerization than for 4-methyl-1-pentene homopolymerization. Similarly, **2**/MAO is 90 times more active for ethylene homopolymerization than for 1-octene homopolymerization.⁸ Adjusting the homopolymerization values in Table 1 for monomer concentration reveals that **1**/MAO is merely 2 times more active with ethylene than with 4-methyl-1-pentene, despite the fact that the latter is a branched α -olefin.

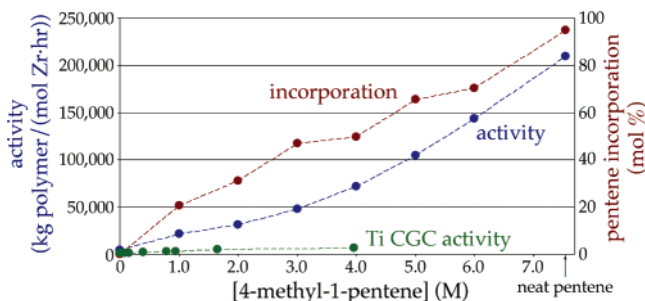


Figure 2. Activity and 4-methyl-1-pentene incorporation with **1**/MAO are proportional to comonomer concentration in ethylene/4-methyl-1-pentene copolymerizations ($T_p = 75\text{ }^\circ\text{C}$; 80 psi ethylene in toluene). The activity response of $\text{Me}_2\text{Si}(\eta^5\text{-2,3-Me}_2\text{-benz[e]Ind})(\eta^1\text{-N-}i\text{Bu})\text{TiCl}_2/\text{MAO}$ is shown for comparison.⁶

Astoundingly, the activity for ethylene homopolymerization is *one-sixth* that of 1-octene homopolymerization. Indeed, **1**/MAO can exhibit an *inverted preference for α -olefin homopolymerization over ethylene homopolymerization*. We know of no precedent for this tendency.

Table 1 also highlights the copolymerization ability of **1**/MAO. As long as ethylene is present, the copolymerization activity of **2**/MAO is comparable to that of **1**/MAO. However, when 4-methyl-1-pentene and 1-octene are copolymerized by **1**/MAO, the activity is less than when ethylene is present but, nonetheless, is 52 times more active than with **2**/MAO and easily excels that of any known CGC for the copolymerization of two bulky α -olefins. These findings further emphasize the unusually high reactivity of **1**/MAO toward α -olefins.

Although some ethylene polymerizations initially exhibit a measurable increase in activity upon introduction of an α -olefin (the *comonomer effect*),¹⁴ the *overall trend* for homogeneous Ziegler–Natta olefin copolymerization systems invariably reveals a diminished activity as α -olefin concentration further increases. **1**/MAO operates contrary to this trend. In ethylene/4-methyl-1-pentene copolymerizations with **1**/MAO, *the activity follows an approximate linear relationship with 4-methyl-1-pentene concentration at all concentrations, including neat comonomer*. Figure 2 illustrates this relationship and also indicates the mol % of 4-methyl-1-pentene incorporated into the polymers. In neat comonomer, 4-methyl-1-pentene incorporation (>95%) is comparable to or greater than its feed fraction (ca. 94%). Figure 3 illustrates a similar *unyielding comonomer effect* for ethylene/1-octene copolymerizations with **1**/MAO, for which activities are even greater.

In summary, the sterically expanded catalyst system of **1**/MAO produces homopolymers and copolymers of α -olefins with unprecedented activities and incorporation rates. A tentative explanation to be investigated is that the spatial accessibility of **1** renders a sterically indiscriminate catalyst and selectivity then defaults to electronic considerations, which favor coordination and insertion of the more electron-rich α -olefins over ethylene.

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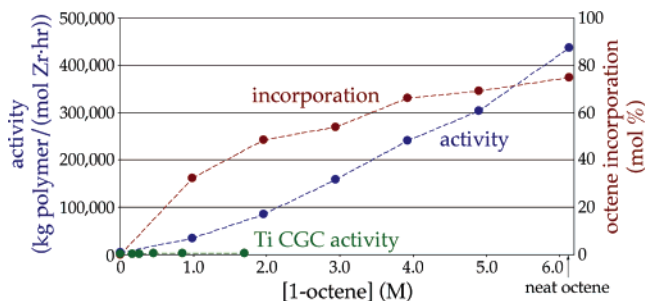


Figure 3. Activity and 1-octene incorporation with **1**/MAO are proportional to comonomer concentration in ethylene/1-octene copolymerizations ($T_p = 75\text{ }^\circ\text{C}$; 80 psi ethylene in toluene). The activity response of $\text{Me}_2\text{Si}(\eta^5\text{-2-Me-benz[e]Ind})(\eta^1\text{-N-}i\text{Bu})\text{TiCl}_2/\text{MAO}$ is shown for comparison.⁸

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Supporting Information Available: Synthesis and characterization data for **1** as well as polymerization details and polymer characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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